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(54) A thickening agent and cosmetic compositions containing it

(57) A gelling or thickening agent is produced from the ionic interaction of:

a cationic polymer comprising a polymer of a cellulose, or a cellulose derivative, which is grafted with a quaternary ammonium salt of a water-soluble monomer, and

a carboxylic anionic polymer having a specified capillary viscosity and Epprecht-Drage viscosity.

The anionic polymer may be polymethacrylic acid, a copolymer of methacrylic acid with an alkyl acrylate or methacrylate, an acrylamide derivative, maleic acid, a monoalkyl maleate or N-vinyl pyrrolidone, or an ethylene-maleic anhydride copolymer.

The agent is incorporated in compositions for treating the hair, skin or nails e.g. hair rinsing or setting lotions, shampoos, anti dandruff compositions, anti seborrhoeic compositions, support gels for permanent waving, hair dyeing compositions, anti-acne compositions and antipsoriatic compositions.

SPECIFICATION

| | A thickening agent and cosmetic compositions containing it | |
|----|--|------|
| 5 | The present invention relates to a new gelling or thickening agent, new thickened or gelled cosmetic compositions containing such an agent and a process enabling cosmetic compositions to be gelled and/or thickened. | . 5 |
| 10 | A general requirement existing in the cosmetics industry is for compositions for hair or for the skin which do not flow too quickly; such is the case, in particular, with the compositions | . 10 |
| 15 | In previous patents such as French Patents 2,383,660, 2,505,179 and 2,542,997, we have already described compositions containing cationic polymers and anionic polymers in an aqueous medium capable of being presented in the form of thickened or gelled compositions. The polymers are employed in these compositions in order to impart to hair advantageous shape-retention, sheen and disentangling properties. These compositions are optionally thickened with a | 15 |
| 20 | gelling or thickening agent which is added to the polymers. Such gelled or thickened compositions of the prior art have the disadvantage, however, resulting from the presence of the gelling or thickening agents, of excessively loading the hair or of leaving an unattractive powdery deposit or, yet again, of imparting to it an unpleasant feel or a dull appearance, particularly when involving compositions whose application is not followed by a rinse. | 20 |
| 25 | | 25 |
| 30 | positions conferring onto hair the advantageous shape-retention and sheen properties of the compositions containing cationic and anionic polymers, while avoiding the abovementioned disadvantages due to the addition of gelling agents or thickeners. It is known to form gels from a polymer derived from a quaternary ammonium of cellulose ether as described in US-A-3,472,840 and from an anionic polymer which is alginic acid or a | 30 |
| 35 | polysulphonic acid such as 2-acrylamido-2-methylpropanesulphonic acid. The gelled compositions produced in this manner result, on the one hand, from the use of anionic polymers which themselves have thickening or gelling properties and, furthermore, require relatively high solids concentrations. Furthermore, such compositions are not completely satisfactory when they are employed for conditioning hair damaged by physical or chemical treatments or by atmospheric | 35 |
| 40 | agents. We have found that it is possible to prepare aqueous cosmetic compositions which are gelled or thickened by a copolymer of cellulose or of a cellulose derivative which are grafted by a radical route with a quaternary ammonium salt of a water-soluble monomer with certain carboxy- | 40 |
| 45 | lic anionic polymers. This synergistic effect appears to be due, though this is merely a hypothesis, to the formation of an interpolymer by ionic interaction in an aqueous medium. To make the definition easier, the term "thickener" or "thickening agent" is employed in the remainder of the specification to denote a product having thickening and/or gelling properties resulting from this interaction. | 45 |
| 50 | The formation of a thickening agent is particularly surprising insofar as it results from polymers which do not individually have the thickening properties of the resulting agent. This capacity is markedly superior to that of gels known previously, some of which have been produced using anionic polymers which themselves have gelling properties. This is particularly advantageous within the scope of the present invention because the thickening characteristics make it possible | 50 |
| 55 | not only to achieve a saving in the use of the polymers to obtain an identical gelling but at the same time make it possible to impart to the hair or to the skin, which are treated with these compositions, certain improved cosmetic properties without loading the hair excessively. The cosmetic compositions containing the thickening agent have the advantage of not loading the hair, even when the applications are repeated, especially in the case of compositions which | 55 |
| 60 | are applied using methods which do not involve a rinsing stage, and of imparting a pleasant feel and a gleaming appearance to the hair. They impart good shape retention and good liveliness to hair, and more particularly to fine hair, in the case of the compositions whose application is followed by a water rinse. Lastly, these compositions make it possible to improve the treatment | 60 |

followed by a water rinse. Lastly, these compositions make it possible to improve the treatment of damaged hair, especially insofar as its disentangling, its softness and its feel are concerned. The subject of the present invention concerns a thickener resulting from an ionic interaction in an aqueous medium of a copolymer of a cellulose or a cellulose derivative grafted by a radical 65 route with a quaternary ammonium salt of a water-soluble monomer with a particular group of

carboxylic anionic polymers. The present invention provides a gelling or thickening agent produced from the ionic interaction of: a cationic polymer comprising a polymer of cellulose or a cellulose derivative which are grafted 5 with a quaternary ammonium salt of a water-soluble monomer, and a carboxylic anionic polymer having an absolute capillary viscosity, at a concentration of 5% in dimethylformamide or methanol at 30°C, of lower than or equal to 30 x 10⁻³ Pa s, this thickener having an Epprecht-Drage viscosity, module 3, of at least 0.45 Pa s in solution at a concentration of 1% in water at 21°C. The ionic interaction is preferably carried out in an aqueous medium and the grafting is 10 preferably carried out by a radical route. The cationic polymer preferably has an absolute capillary viscosity at 1% in water at 30°C of less than 0.025 Pa s. The cationic polymer is preferably a cellulose, or hydroxyalkyl cellulose such as hydroxymethyl cellulose, hydroxyethyl cellulose or hydroxypropyl cellulose which are grafted by a radical route 15 with a methacryloylethyltrimethylammonium, methacrylamidopropyltrimethylammonium or dimethyldiallylammonium salt, more particularly a halide such as a chloride, or a methosulphate. A particularly preferred cationic polymer is a hydroxyethyl cellulose copolymer grafted by a radical route with diallyldimethylammonium chloride sold under the trade name "Celquat L 200" or "Celquat H 100" by National Starch, which is also called "Polyquaternium 4" in the CFTA 20 20 dictionary. When diluted to a concentration of 1% in water at a temperature of 30°C, this polymer has an absolute capillary viscosity of the order of 0.01 Pa s in the case of the product marketed under the trade name "Celquat L 200" or of 0.021 Pa s in the case of the product marketed under the trade name "Celquat H 100". The carboxylic anionic polymer preferably has a molecular weight of from 500 to 3,000,000 25 25 more particularly from 1,000 to 3,000,000. It is preferably a film-forming polymer. Particularly preferred polymers are: (a) a methacrylic acid homopolymer which has a molecular weight of greater than 20,000, as determined by light scattering. (b) a copolymer of methacrylic acid with one of the following monomers: 30 C,-C, alkyl acrylate or methacrylate; an acrylamide derivative, such as N,N-dimethylacrylamide, diacetoneacrylamide or N-tert-butylacrylamide; maleic acid; C₁-C₄ monoalkyl maleate; or 35 N-vinylpyrrolidone; or (c) a copolymer of ethylene with maleic anhydride, such as the product sold under the trade name EMA 31 by Monsanto Cie. Particularly preferred anionic polymers are methacrylic acid copolymers which have an absolute capillary viscosity measured at a concentration of 5% in solution in dimethylformamide or 40 40 methanol, at 30°C, of from 0.003 to 0.030 Pa s, more particularly a copolymer of methacrylic acid with methyl methacrylate whose absolute capillary viscosity, measured at a concentration of 5% in solution in dimethylformamide, is of the order of 0.015 Pa s or a copolymer of methacrylic acid with monoethyl maleate which has an absolute capillary viscosity, measured at a concentration of 5% in solution in dimethylformamide, of the order of 0.013 Pa s, a copolymer 45 of methacrylic acid with butyl methacrylate whose absolute capillary viscosity, measured at a 45 concentration of 5% in solution in methanol, is of the order of 0.010 Pa s, or a copolymer of methacrylic acid with maleic acid whose absolute capillary viscosity, measured at a concentration of 5% in solution in dimethylformamide, is of the order of 0.016 Pa s. The thickener may, for example, be prepared under the following conditions: a quantity of water is added to the copolymer of cellulose or cellulose derivative grafted by a radical route with a quaternary ammonium salt of a water-soluble monomer to dissolve it (solution 1). Separately, a quantity of water is added to the carboxylic anionic polymer to dissolve it, the dissolution being promoted by neutralization with a conventional alkalifying agent such as aque-55 55 ous ammonia or an alkanolamine (solution II). The thickener may then be formed by adding solution I to solution II or vice versa, with stirring, at ambient temperature. When the gelling or thickening agent-has formed it can then, if desired, be diluted with water or with a mixture of water and alcohol, the proportion of alcohol being that required to produce the required alcoholic strength for the formulation. 60 According to an alternative form of this process, it is equally possible, without recourse to neutralization, to dissolve the carboxylic anionic polymer in alcohol, preferably ethanol, at a concentration such as to bring the final formulation to the alcoholic strength required. The thickener may also be formed in the aqueous cosmetic medium itself.

The copolymer of cellulose or a cellulose derivative which are grafted with a quaternary 65 ammonium salt is preferably used in an aqueous medium, generally in an amount of from 0.01

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| | | |
|----|---|-------------|
| | to 6%, especially 0.1 to 1.5%, by weight relative to the weight of the composition. The carboxylic anionic polymer is preferably used in an aqueous medium, generally in an amount of from 0.01 to 6%, especially 0.1 to 1.5%, by weight relative to the weight of the composition. The weight ratio of the cationic polymer to the carboxylic anionic polymer is preferably from 1:5 | |
| 5 | to 5:1, more preferably from 1:2 to 2:1 and is especially equal to about 1:1. The present invention also provides a cosmetic composition suitable for the treatment of hair, skin or nails which comprises at least one gelling or thickening agent as defined above and at least one further adjuvant. | 5 |
| 10 | The thickener is preferably present in the composition of the present invention in a concentration of from 0.02 to 12%, more preferably from 0.2 to 3%, by weight based on the total weight of the composition. | 10 |
| 15 | This composition is generally in aqueous form, but may contain other cosmetically acceptable solvents such as, for example, lower (for example C_1 — C_8 or C_1 — C_4) alcohols such as ethanol or isopropanol, glycerol, glycols or glycol ethers such as ethylene glycol monobutyl ether, propylene glycol, diethylene glycol monoethyl ether and monomethyl ether, in proportions which do not | 15 |
| | affect the formation of the thickener. These compositions have a pH which is generally from 6 to 12, preferably from 6.5 to 9, more particularly, close to neutrality, for example of the order of 7 to 8. | |
| 20 | The pH may be adjusted with an alkalifying or acidifying agent which is usually employed in the field of cosmetics. The cosmetic composition may, for example, be employed as a shampoo, after-shampoo | 20 |
| , | composition, product for rinsing to be applied before or after shampooing, before or after dyeing or bleaching, before or after permanent-waving or hair straightening, a hair-setting or blow-drying composition, a restructuring composition, or a support for permanent-waving or for dyeing or | Ω |
| 25 | bleaching hair. The composition may also contain a dermatological active principle such as an antidandruff, antiseborrhoeic, antiacne, antifungal, bactericidal, keratolytic or antipsoriatic agent. When the composition is in the form of a thickened lotion or gel for hair-setting or for blowdrying, it may optionally contain other polymers which are usually employed in a composition of | 25 |
| 30 | this type, more particularly nonionic polymers such as polyvinylpyrrolidones, copolymers of polyvinylpyrrolidone with vinyl acetate, or anionic polymers which do not have the abovementioned properties of gelling or thickening with the cationic polymer, for example copolymers of vinyl acetate with an unsaturated carboxylic acid such as crotonic acid, copolymers resulting | 30 |
| 35 | from the copolymerization of vinyl acetate with crotonic acid and an acrylic or methacrylic ester, copolymers resulting from the copolymerization of vinyl acetate with an alkyl vinyl ether and an unsaturated carboxylic acid and copolymers resulting from the copolymerization of vinyl acetate with crotonic acid and a vinyl ester of an acid containing a long carbon chain or an allyl or methallyl ester of an acid containing a long carbon chain. These polymers are generally em- | 35 |
| 40 | ployed in a concentration of from 0.1 to 5% by weight based on the total weight of the composition. | 40 |
| 40 | agents such as quaternary proteins, cationic silicone polymers, cationic surfactants and cationic polymers other than polymers of cellulose or of cellulose derivatives grafted by a radical route with a quaternary ammonium water-soluble monomer, of the polyamine, polyaminoamide or quaternary polyammonium type. | 1 |
| 45 | When the compositions are employed as shampoos, they may contain surface-active agents with detergent properties which are known per se, such as anionic, cationic, nonionic or amphoteric surface-active agents or mixtures thereof. In general, the surface-active agents are present in a proportion of from 0.1 to 30% by weight | 45 |
| 50 | based on the total weight of the composition. | 50 |
| 55 | The compositions may also be used for conditioning skin and nails. A particularly perferred cosmetic composition is a hair-shaping composition which is not rinsed off. This composition comprises, in an aqueous or aqueous-alcoholic medium, a thickener resulting from the ionic interaction of 0.1 to 1.5% by weight of a hydroxyethyl cellulose copolymer | .55 |
| | grafted by a radical route with diallyldimethylammonium chloride and 0.1 to 1.5% by weight of a copolymer of methacrylic acid with methylmethacrylate or with monoethyl maleate or with butyl methacrylate whose absolute capillary viscosity, measured at 30°C in solution in dimethylformamide or methanol at a concentration of 5%, is from 0.010 to 0.015 Pa s, the Epprecht-Drage | |
| 60 | viscosity of the thickener, measured at 21°C, module 3, diluted to a concentration of 1% in water, being higher than 0.45 Pa s, and the pH of the composition being from 6.5 to 9. The compositions according to the invention may contain any other ingredient which is usually employed in cosmetics, such as perfumes, colourants, preservatives, sequestering agents, sof- | 60 |
| 65 | teners or silicones. | 65 |

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wherein at least one thickener as defined above or a composition containing the polymers forming the thickener in a proportion of from 0.02 to 12% by weight based on the total weight of the composition is introduced into the composition to give it an Epprecht-Drage viscosity, measured at 21°C (module 3), of at least 0.450 Pa s.

Aqueous gels or thickened compositions containing the thickener may be prepared separately, and the cosmetic composition may be prepared in a different step, if desired at the time of use.

The present invention also provides a process for the treatment of hair, of the skin and of the nails, wherein a cosmetic composition as defined above is applied thereto, it being possible for this composition to be rinsed off with water, or not, according to the nature of the treatment 10 desired.

We have found that the composition for the treatment of hair not only makes it possible to localize the product on hair properly without flowing onto the face but that the hair treated in this manner also has a pleasant feel and a shiny appearance. Furthermore, the thickened or gelled composition has the advantage of being clear.

15 The examples which follow further illustrate the invention.

EXAMPLE 1

Aqueous gels were prepared according to the information which appears in Table A which follows. For this purpose 50 cm³ of an aqueous solution containing 1% of active substance of 20 the product marketed under the trade name of "Celquat L 200", which is a copolymer of hydroxyethyl cellulose grafted by a radical route with diallyldimethylammonium chloride, were added at ambient temperature and with mechanical stirring to 50 cm³ of an ethanolic solution at an alcohol strength of 20° containing 1% as active substance of the previously neutralized anionic polymer defined in the table.

25 In Table A below, the measurement of the absolute capillary viscosity of the anionic polymers is carried out in dimethylformamide (DMF) and/or in methanol.

45

TABLE A

| | INITIAL MIXTURE | | | • | Epprecht-Drage viscosity | |
|---------------|---|---|----------|-------|---------------------------------|--|
| | CATIONIC POLYMER | Absolute capillary viscosity Pa s x 10 ⁻³ | | | of the thickener formed Pas (3) | |
| CELQUAT L 200 | | : ", | (1) 10.4 | | | |
| | CARBOXYLIC ANIONIC POLYMER | Propor- | (2) DHP | сизов | | |
| | Methacrylic acid/methyl, methacrylate copolymer | 50/50 | 15 | | 1-550 | |
| | | 80/20 | 24-47 | 10.56 | 1-430 | |
| ļ | Retherrylic acid/methyl acrylate cocolymer | 50/50 | | 16-4 | 1, 300 | |
| | 4 | 80/20 | 17.7 | 4.5 | 1, 150 | |
| | Methacrylic acid/butyl methacrylate copolymer | 65/15 | "" | 9-94 | 2,000 | |
| | Methacrylic acid/monoethyl melente copolymer | 63-6/ 36-4 | 3,46 | | 0.620 (mod 4) | |
| 1 | | . 59/41 | 8 | 1 | 1-000 (mod 4). | |
| | • | 66/34 | 19 -2 | | 0.780;1,500 (mod 4) | |
| I | • | 61/39 | 26.8 | Ì | 0-580;1-250 (mod 4) | |
| | * * * * * * * * * * * * * * * * * * * | 62/38 | 10-4 | | 0.550;1.000 (mod 4) | |
| | * * * | 65/35 | 14,1 | | 0.800/1.200 (mod 4) | |
| | | 63/37 | 13 | | 1.490;2.000 (mod 4) | |
| | • | 66/34 | 13 | | 1.70012_100 (mod 4) | |
| | | 68/32 | 19.2 | | 1.700;2.500 (mod 4) | |
| | * | 72/29 | 14.2 | | 1. 381:1, 500 (mod 4) | |
| | Methacrylis:acid/M,M-dimethylacrylewide copolymer | 50/50 | | • | 0.900 | |
| | | 80/20 | 16-3 - | | 1-350 | |
| | Rethacrylic acid/discetonescrylamide copolymer (4) | 80/20 | | 1,07 | 1-200 | |
| | Methacrylic acid/N-tert-butylacrylamide copolymer | 80/20 | l | 4.06 | 1-050 | |
| | Methacrylic scid/maleic acid copolymer | 65/35 | 16.7 | | 2-100 | |
| 1 | | 70/30 | 13-6 | | 1-900 | |
| | Methacrylic acid/N-vinylpyrrolidone copolymer | 80/20 | 9-2 | | 1-050 | |
| | Polymethecrylic acid FM 137,000 | | | 6.8 | 1.400 | |
| | " " Mi 186,000 | | | 9.8 | 2-100 | |
| | Ethylene/saleic anhydride copolymer Ronsanto EMA 31 | 1 | 9-42 | 8-15 | 1-600 | |

⁽¹⁾ measured at 30°C in %% strength solution in water

⁽²⁾ measured at 30°C in SX strength solution in dimethylformamide or methanol

⁽³⁾ module 3 - measured at 21° C in 1% strength 10° aqueous alcohol solution - pH = 7.5

⁽⁴⁾ viscosity measured using a 1% strength solution of this anionic polymer.

EXAMPLES 2 to 11

The following gelled compositions for hair styling are prepared (Tables B and C).

When these various compositions are applied to clean wet hair, they impart shape retention to it without leaving a powdery deposit. When they are applied to dried hair it is found that the composition makes styling easier without loading the hair and that, once dried, the latter is soft and has a pleasant feel.

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10

| *** COMPOSITIONS | | EXAMPLE No. | | | | | |
|--|-------|-------------|-------|----------|--------|------|--|
| | (2 | 3 | 4 | 5 | 6 | 15 | |
| Celquat H 100 | 0.5 | 0.4 | | | | | |
| Celcuat L 200 g I AS | ٠ . | | 0.8 | | 0-3 | 20 | |
| Methacrylic acid/monoethyl maleate copolyme (66/34) g % AS | 0.5 | 1. | | · | | ŀ | |
| Methacrylic acid/maleic acid copolymer (70/30) g % AS | | 0.6 | | <i>'</i> | | 25 | |
| Methacrylic acid/butyl methacrylate copolym (85/15) g X AS | er · | | 0.8 | | | | |
| Polymethacrylic acid NW 137,000 g % AS | | ' | | | 0.4 | | |
| Ethylene/maleic anhydride copolymer Monsanto EMA 31 g % AS | 1 | | | 0.8 | | . 30 | |
| 2-Amino-2-methyl-1-propanol q.s. pH | 8 | 9 | 7 | 6 | 9 | | |
| Ethyl elcohol Q.S. | 20" | | 25* | | 10° | 35 | |
| Nater q.s. g | 100 | 100 | 100 | 100 | 100 | · | |
| Epprecht-Drage viscosity 21°C 1% in H ₂ O (accule 3) in Pa s | L 150 | g. 700 | 2 450 | 2,400 | 0 .725 | 40 | |

TABLE C

| | | | | | 7 |
|--|-----------------------|----------|--|------------|-----------|
| COMPOSITIONS | | В | EXAMPLE | 10 | 1 11 |
| Celcust H 100 | | • | | 10 | |
| g I AS | 0.4 | | | 0.5 | · · |
| Celouat L 200 g X AS | | 1 | 0.66 | | 0,33 |
| Methacrylic acid/N-tert-butylacrylamide 80/20 g X AS | copolymer 0-2 | | | | |
| Methacrylic scid/M,N-dimethyl scrylamide 20/20 o X AS | copolymer | 0-5 | 1 | | , |
| Methacrylic acid/methyl methacrylate copo 50/50 g X AS | olymer | 1 | 0.33 | | |
| Methacrylic acid/methyl methacrylate cope 80/20 g X AS | olymer | İ | | ١. | |
| Polymethacrylic acid MW 186,000 | | | | 1. | |
| g X AS | i . | | | | 0.66 |
| | | | | | |
| 2-Amino-2-methyl-1-propenol | | 8.5 | 7.5 | 8-5 | 2.5 |
| q.s. pH Ethyl alcohol | | 1 | | 10° | 10° |
| Q.S. Perfuse, colorant, preservative | | 30° | 10°. | 10 | 1.0 |
| Vater q.s. g | 100 | 100 | 100 | 100 | 100 |
| Epprecht-Drage viscosity 21°C 1% in H ₂ O (module 3) in Pa s | 0.480 | 1 600 | 0.900 | 1, 725 | 1, 300 |
| 112 310 1090 | - | 1 | | | |
| EXAMPLE 12 | | | | • | |
| An after-shampoo of the following con | | _ | | | |
| A) Celquat L 200 from National Starch B) 72/28 Methacrylic acid/monoethyl n | | As | | | |
| copolymer | | As | | | |
| Distearyldimethylammonium chloride Hydrochloric acid q.s. pH: | 1 g | | | | |
| Water q.s. | 100 g | | | | |
| This composition is applied to clean, reninutes it is rinsed off with water. The vand has body. | | | | | |
| The gel obtained by interaction of the | | | | cht-Drag | e viscosi |
| at 21°C, module 3, of 1.7 Pa s at a con- | centration of 1.4% in | n water | • | | |
| EXAMPLE 13 | | | | | |
| An after-shampoo of the following con | | | | | |
| A) Celquat L 200 from National Starch B) 50/50 Methacrylic acid/methyl meth | | AS | | | |
| copolymer | • | AS | • | | |
| Quaternized protein sold under the trace | | ۸۵ | | | |
| name of "Lexein QX 3000" by Inolex Hydrochloric acid q.s. pH: | | AS. | | | |
| Water q.s. pri. | 100 g | | | | |
| | | | | | |
| This gelled composition is applied to c | lean, roughly dried h | air. Aft | er being | left in pl | ace for a |
| few minutes it is rinsed off with water. | | | | | |
| | | | | | |
| The dried hair is lively and has body. The gel obtained by interaction of the | nolymers A and P h | 26 2n C | nnracht-l | Drane vie | cosity et |

| | | | • | • 1 | | |
|------|--|-------------|-----------------|--------------------------|-----------------------|---------|
| | EXAMPLE 14 | | | • | | |
| | The following shampoo is prepared: | | | | • . | • |
| | (A) Celquat L 200 from National Starch | 0.5 | g AS | 3 | | |
| 5 | (B) 50/50 Methacrylic acid/methyl methacrylate | • | • | • | | 5 |
| | copolymer | 0.7 | g AS | 3 | j | • |
| | Nonionic surfactant of formula: | | | | | |
| | | | | • | | • |
| 40 | R-CHOH-CH ₂ O-[CH ₂ -CHOH-CH ₂ O],-H | | • | | | 10 |
| 10 | in which | | | | • | |
| | R denotes a mixture of C ₉ -C ₁₂ alkyl radicals | | | | • | |
| | n denotes a statistical mean value of | | • | | | |
| | about 3.5 | 10 | g AS | 5 | | 46 |
| 15 | Hydrochloric acid q.s. pH: 7.4 | | | | | 15 |
| | Perfume, preservative q.s. | 100 | _ | | | |
| | Water | . 100 | .9 | | | |
| | This shampoo has the appearance of a clear g | el. | | | • | F |
| 20 | | s A and | B has | an Epprech | t-Drage viscosity at | 20 |
| 20 | 21°C, module 3, of 1.65 Pa s at a concentration | of 1% i | n wate | er. | _ | |
| | | | | | • | |
| | EXAMPLE 15 | | | | | |
| | The following shampoo is prepared: | 0.7 | ~ A S | 2 | • | 25 |
| 25 | (A) Celquat L 200 from National Starch (B) 72/28 Methacrylic acid/monoethyl maleate | 0.7 | g AS | • · | • | |
| | copolymer copolymer | 0.7 | g AS | 3 | | |
| | Sodium alkyl ether carboxylate oxyethylenated | | | • | • | 1 |
| | with 3 moles of ethylene oxide, sold by | | • | | | |
| 30 | | | 1 | _ | • | 30 |
| | 2747/30" | 10 | g AS | S | y | |
| | Hydrochloric acid q.s. pH: 6 | • | | | | |
| | Perfume, preservative q.s. | 100 | g . | | | |
| 35 | Water q.s. | 100 | 9 | | | . 35 |
| 39 | This shampoo has the appearance of a clear g | iel. | | | | |
| | The gel obtained by interaction of the polymer | rs A and | B has | an Epprech | t-Drage viscosity at | |
| | 21°, module 3, of 1.7 Pa s at a concentration of | f 1.4% ir | n wate | er. | • | |
| | | | | • | • | 40 |
| . 40 | EXAMPLE 16 | | • | | | . 40 |
| | The following lotion is prepared: | 0.1 | g | | · | • |
| | (A) Celquat L 200 (B) Polymethacrylic acid | 0.1 | g | | | |
| | 2-Amino-2-methyl-1-propanol q.s. pH: 7.5 | | J | | | |
| 45 | | | | | | 45 |
| | Water q.s. | 100 | g | | • | |
| | | | ·· ! | | | |
| | This hair-setting lotion is slightly gelled and do The gel obtained by interaction of the polymer | re A and | equire R hac | rinsing. : an Engrech | t-Drage viscosity at | • |
| E0 | 21°C, module 2, of 0.095 Pa s at a concentration | on of 0.2 | % in 1 | water. | t bidge tiecesity as | 50 |
| D. | 21 C, Module 2, or 0.000 10 0 00 0 0000 | | .,. | | | |
| | EXAMPLE 17 | | | | | |
| | The following antidandruff composition is prep | ared: | | | | |
| | (A) Celquat L 200 | 1,5 | g | £ | | 55 |
| . 55 | (B) 66/34 Methacrylic acid/monoethyl maleate | 4.2 | _ | | • | 33 |
| | copolymer | 1.2 | 9 | | ÷ . | • |
| | 1-Hydroxy-4-methyl-6-(2,4,4-trimethylpentyl)- 2-(1H)-pyridinone, ethanolamine salt, sold unde | or | | | | |
| | the trade name "Octopirox" by Hoechst | 0.1 | g | | | |
| 60 |) Ethyl alcohol q.s. 30° | J. . | 0 | | • | 60 |
| J | 2-Amino-2-methyl-1-propanol q.s. pH 7 | | | | | |
| | Preservative, perfume q.s. | | | • | | |
| | Water q.s. | 100 | g | | | |
| | | | | | oos not require rinei | na. 65° |
| . 6 | This antidandruff composition has the appeara | ince of a | ciear | ger and it d | oes not tedana tingi | |
| | | | | | | |

| • | • | | | | | | |
|----|--|--|------------------------|--------------|-----------------------------|--------------------------------------|--------------|
| | The gel obtained by interaction 21°C, module 3, of about 1.8 F | on of the polymers as at a concentr | A and ation of | B has 2.7% | an Epprecht in water. | -Drage viscosity | at · |
| 5 | (A) Celquat L 200 | | epared: 0.5 | g | | | 5 |
| | (B) 50/50 Methacrylic acid/me copolymer | thyl methacrylate | 0.5 | g | | * | |
| 10 | | • • | 1' | g | | d y | 10 |
| | Preservative, perfume Water | q.s q.s. | 100 | g | | | |
| 15 | This antiseborrhoeic composit ance of a clear gel and does no The gel obtained by interactio 21°C, module 3, of about 1.2 P | t require rinsing. In of the polymers | A and | B has | an Epprecht- | | 15 |
| | EXAMPLE 19 | | | | | | , |
| 20 | The support gel for permanen Composition 1 | t-waving, of the f | ollowing | compo | osition, is pr | epared: | 20 |
| | Glycerol monothioglycolate Glycerin | q.s. | 68.3 100 | g g | | . 191 | |
| 25 | Composition 2 Celquat L 200 | | 1.8 | g | | | 25 |
| | 70/30 Methacrylic acid/maleic copolymer | | 1.5 | 9 | | | |
| | 2-Amino-2-methyl-1-propanol Triethanolamine | | 3 | 9 | • | | • |
| 30 | Perfume, colorant, preservative Water | q.s. q.s. | 100 | 9 | | | 30 |
| | The two compositions 1 and | 2 are mixed ad ho | oc in pro | portion | ns of 32 g c | of composition 1 | to |
| 35 | 87 g of composition 2. This mixture is applied to hair in place, it is rinsed off and an 3, is applied for 10 minutes. | which is wound o | onto roll consistir | ers, for | r 15 minutes -volume hyd | s. After 15 minut rogen peroxide, | tes 35 pH |
| | The hair is then rinsed. | | | | | | -3:- |
| 40 | EXAMPLE 20 | | | | | | 40 |
| | The following direct-dyeing co 50/50 Methacrylic acid/methyl r copolymer | mposition is preparent methacrylate | | | | | |
| 45 | Celquat L 200 from National Sta 1-N-(y-hydroxypropyl)amino-2-niti | | 0.5 0.5 | g AS g AS | | | 45 |
| | bis(β-hydroxyethyl)aminobenzer chloride | • | 0.1 | g | | • | |
| | 2-Amino-2-methyl-1-propanol Ethyl alcohol | q.s. pH 7.5 q.s. 10° | | 3 | | | |
| 50 | Preservative | q.s. q.s. | 100 | g | | | 50 |
| | | • | | - | | | |

This dyeing composition is applied to wet brown hair, washed beforehand. After drying, the hair acquires an ashen brown color.

| 5 | EXAMPLE 21 The antipsoriatic composition the gel of the following composition (A) Celquat L 200 (B) 50/50 Methacrylic acid/mecopolymer 2-amino-2-methyl-1-propanol Ethyl alcohol Preservative Water | sition: ethyl methacrylate | 0.5 0.5 0.5 | 5 g of anthr g g | aline at the | e time of use to | 5 |
|----------|---|---|---|--|--|--|-----------|
| 15 | The antipsoriatic composition The gel obtained by interactic 21°C, module 3, of about 1.2 i | on of the polymers | A and | B has an Ei | oprecht-Dra | ing. age viscosity at | 15 |
| 20 | EXAMPLE 22 The following antiacne composition is applied to | sition is given in E | by addi xample | ng 5 g of b 21. | enzoyl per | oxide at the time | 20 |
| 25 | EXAMPLE 23 The following bactericidal comphenoxy) phenol or triclosan (DC to the gel whose composition is This composition is applied to | sold under the named s given in Example | ame of | dding 1 g o ''Irgasan Df | f 5-chloro- 300" at | 2-(2,4-dichloro- the time of use | 25 |
| 30 | EXAMPLE 24 A hair-conditioning composition of water to 46 g of a gel of the (A) Celquat L 200 | e following compos | ndding 1 sition: 4.5 | 18 g of iris | powder dil | uted with 36 g | : . 30 |
| 35 | (B) 80/20 Methacrylic acid/N-v copolymer Ethyl alcohol 2-Amino-2-methyl-1-propanol Perfume, preservative Water | q.s. 10° q.s. pH 7.5 q.s. | 4.5 100 | g | | | 35 |
| 40 | The composition is applied to The gel obtained by interactio 21°C, module 4, of 11.7 Pa s a | n of the polymers | A and | B has an Ep | as a soft f precht-Dra | eel. ge viscosity at | 40 |
| 45 | EXAMPLE 25 The following restructuring rin ourea at the time of use to the This composition is applied to | gel of Example 21 | ered by at pH | adding 1.5 6. | g of dimet | hylolethylenethi- | 45 |
| 50 | CLAIMS 1. A gelling or thickening age a cationic polymer comprising grafted with a quaternary ammo a carboxylic anionic polymer hidimethylformamide or methanol | a polymer of a cel nium salt of a wate aving an absolute of at 30°C, of lower to | llulose d er-solub capillary than or | or a cellulos le monomer viscosity, a equal to 30 | e derivative r, and at a concei x 10 ⁻³ Pa | ntration of 5% in s, this thickener | 50 |
| 55 60 | having an Epprecht-Drage viscos tion of 1% in water at 21°C. 2. An agent according to cla copolymer grafted by a radical r monomer which is a methacrylo ium or dimethyldiallylammonium 3. An agent according to cla a methacrylic acid homopolym | ity, module 3, of a im 1 wherein the c oute with a quater ylethyltrimethylamm salt. im 1 or 2, wherein | at least ationic nary am nonium, | O.45 Pa s in polymer is a monium sal methacrylar rboxylic anic | n solution a hydroxya t of a wate midopropyl onic polyme | at a concentra- lkyl cellulose er-soluble trimethylammon- er is: | 55 60 |
| 65 | by light scattering, a copolymer of methacrylic ac derivative, maleic acid, a C ₁ -C ₄ i a copolymer of ethylene with | id with a C₁–C₄ alk monoalkyl maleate | yl ecryl | ate or meth | acrylate, ar | , | 65 |

| | 4. An agent according to any one of claims 1 to 3 wherein the anionic polymer is: a copolymer of methacrylic acid with methyl methacrylate whose absolute capillary viscosity, measured in solution in dimethylformamide at a concentration of 5% at 30°C, is of the order of 15×10 ⁻³ Pa s, | |
|----|--|------|
| 5 | a copolymer of methacrylic acid with monoethyl maleate having an absolute capillary viscosity, measured in solution in dimethylformamide at a concentration of 5% at 30°C, of the order of 13×10^{-3} Pa s. | 5 |
| 10 | a copolymer of methacrylic acid with butyl methacrylate whose absolute capillary viscosity, measured in solution in methanol at a concentration of 5% at 30°C, is of the order of 10×10^{-3} Pa s, or | 10 |
| | a copolymer of methacrylic acid with maleic acid whose absolute capillary viscosity, measured in solution in dimethylformamide at a concentration of 5% at 30° C, is of the order of 16×10^{-1} Pa s. | |
| 15 | 5. An agent according to any one of claims 1 to 4 wherein the weight ratio of the cationic polymer to the carboxylic anionic polymer is from 1:5 to 5:1. 6. An agent according to any one of claims 1 to 5 which has been prepared in an aqueous medium comprising 0.01 to 6% of the cationic polymer and 0.01 to 6% of the carboxylic anionic polymer. | 15 , |
| 20 | 7. An agent according to claim 1 substantially as hereinbefore described with reference to any one of the Examples. 8. A cosmetic composition suitable for the treatment of hair, skin or nails, which comprises at least one gelling or thickening agent as defined in any one of claims 1 to 7 and at least one further adjuvant. | 20 |
| 25 | 9. A composition according to claim 8 wherein the gelling or thickening agent is present in a proportion of from 0.02 to 12% by weight based on the total weight of the composition. 10. A composition according to claim 8 or 9, which has a pH of from 6 to 12. | 25 |
| 30 | 11. A composition according to any one of claims 8 to 10 suitable for use as a thickened or gelled lotion for hair-setting or for blow-drying which additionally comprises a nonionic polymer which is a polyvinylpyrrolidone or copolymer or polyvinylpyrrolidone with vinyl acetate, or an anionic polymer which is a copolymer of vinyl acetate with an unsaturated carboxylic acid, a copolymer resulting from the polymerization of vinyl acetate with crotonic acid and an acrylic or methacrylic ester, a copolymer resulting from the copolymerization of vinyl acetate with a vinyl | 30 |
| 35 | alkyl ether and an unsaturated carboxylic acid, a copolymer resulting from the copolymerization of vinyl acetate with crotonic acid and a vinyl ester of an acid containing a long carbon chain or an allyl or methallyl ester of an acid containing a long carbon chain. 12. A composition according to any one of claims 8 to 11 in the form of a shampoo which comprises one or more anionic, cationic, nonionic or amphoteric surface-active agents with a detergent property. | 35 |
| 40 | 13. A composition according to any one of claims 8 to 10, suitable for rinsing off, which comprises a conditioning agent which is a quaternary protein, cationic silicone polymer, cationic surfactant or cationic polymer other than a polymer of a cellulose or cellulose derivative grafted by a radical route with a quaternary ammonium water-soluble monomer. | 40 |
| 45 | 14. A cosmetic composition suitable for use in hair-setting, which comprises, in an aqueous or aqueous-alcoholic medium, a thickener resulting from the ionic interaction of 0.1 to 1.5% by weight of a hydroxyethyl cellulose copolymer grafted by a radical route with diallyldimethylammonium chloride and 0.1 to 1.5% by weight of a copolymer of methacrylic acid with methyl methacrylate or with monoethyl maleate or with butyl methacrylate whose absolute capillary | 45 |
| 50 | viscosity, measured at 30°C in solution in dimethylformamide or methanol at a concentration of 5%, is from 0.010 to 0.015 Pa s, the Epprecht-Drage viscosity of the thickener, measured at 21°C, module 3, diluted to a concentration of 1% in water, being higher than 0.45 Pa s, and the pH of the composition being from 6.5 to 9. | 50 |
| 55 | 15. A cosmetic composition according to claim 8 or 14 substantially as hereinbefore described with reference to any one of the Examples. 16. A process for thickening or gelling an aqueous cosmetic composition wherein at least one thickener as defined in any one of claims 1 to 7 is introduced into the composition to give it an Epprecht-Drage viscosity measured at 21°C (module 3) of at least 0.45 Pa s at a concentration of 1% in water. | 55 |
| 60 | 17. A process for the treatment of hair, of the skin or of the nails, wherein at least one cosmetic composition as defined in any one of claims 8 to 15 or produced by a process as defined in claim 16 is applied thereto. 18. A process according to claim 17 wherein a composition as defined in claim 11 or 14 is applied, this application not being followed by a rinse. | 60 |